Optical phonon behavior in strain-free dilute Ga(As,N) studied by Raman scattering

J. Ibáñez, E. Alarcón-Lladó, R. Cuscó, and L. Artús[a)]
Institut Jaume Almera, Consell Superior d'Investigacions Científiques (CSIC), Lluís Solé i Sabarís s.n., Barcelona 08028, Catalonia, Spain

M. Hopkinson
Department of Electronic and Electrical Engineering, University of Sheffield, S3 3JD Sheffield, United Kingdom

(Received 22 March 2007; accepted 9 May 2007; published online 3 July 2007)

We present a Raman-scattering study on strain-free dilute Ga(As,N) epilayers grown by molecular beam epitaxy. The aim of our work is to discriminate the effect of alloying from the effect of biaxial strain on the frequency behavior of the optical phonon modes of Ga(As,N). In the relaxed epilayers, we observe the following: (i) for the GaN-like LO mode, an upward frequency shift with increasing N which is larger than previously observed in strained samples; (ii) for the GaAs-like LO mode, a redshift with increasing N content which is lower than those reported in the literature on strained samples; and (iii) for the GaAs-like TO mode, we observe a very minor blueshift with increasing N fraction. We discuss the origin of the observed shifts, with particular attention to the reduction of the GaAs-like TO-LO splitting in Ga(As,N). Our data and analysis suggest that such reduction cannot be explained only by a reduction of the total number of Ga–As oscillators due to the substitution of As by N. We discuss the effects of disorder and of ionic plasmon coupling between the GaAs and GaN sublattices of Ga(As,N) on the behavior of the GaAs-like LO mode of the alloy. We conclude that the behavior of this mode is determined by long-range effects. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2749491]

I. INTRODUCTION

Dilute Ga(As,N) alloys and related compounds have recently attracted much attention due to their unique optical properties, which could be exploited to develop optoelectronic devices operating in the 1.3–1.55 μm range of interest for optical fiber communications. Raman spectroscopy is a standard technique to characterize the strain and composition of III-V alloys. Several works have used resonant and nonresonant Raman scattering to investigate dilute $GaAs_{1-y}N_y$ layers.[1–7] In particular, the resonant Raman studies have provided valuable information about the wave function symmetry of the E_- and E_+ subbands of Ga(As,N) observed by reflectance spectroscopy.[3–5]

The optical phonons of Ga(As,N) exhibit a two-mode behavior in the dilute regime. It has been shown that the GaAs-like longitudinal optical (LO) branch of $GaAs_{1-y}N_y$ ($y \lesssim 5\%$) shifts to lower frequencies with increasing y.[1,2,5] In contrast, no appreciable frequency variation with composition of the GaAs-like transverse optical (TO) phonon mode of Ga(As,N) has been observed. The GaN-like LO phonon of Ga(As,N) appears at $\sim 470\ cm^{-1}$ and shifts to higher frequencies with increasing y.[1,4–6] Prokofyeva *et al.*[1] studied a series of strained Ga(As,N) epilayers grown pseudomorphically on GaAs and showed that the downward frequency shifts of the GaAs-like LO mode arise from two different causes: (i) biaxial strain and (ii) alloying effects. The interest of studying relaxed Ga(As,N) layers to confirm that alloying redshifts this mode was recognized in that work.[1] Such type of study on strain-free samples is of particular importance in dilute Ga(As,N) because the elastic constants of this compound might exhibit some deviation from Vegard's law,[8] and this would affect the analysis of the strain-induced phonon frequency shifts in the strained epilayers. Likewise, the frequency shifts observed for the GaN-like LO mode in previous works are likely influenced by biaxial-strain effects. Thus, it would be desirable to study unstrained epilayers in order to discriminate the effect of alloying from that of strain on the frequency behavior of this mode.

In the present work we use the Raman scattering to investigate the behavior of the optical phonons of unstrained dilute $GaAs_{1-y}N_y$. For this purpose, we study a series of relaxed $GaAs_{1-y}N_y$ thick layers grown by molecular beam epitaxy (MBE) on (100)-GaAs substrates (y=0.05%, 0.1%, 0.2%, 0.7%, and 1.5%). To measure the frequency of the forbidden GaAs-like TO modes, we have carried out Raman experiments with the samples tilted about 60° off-normal incidence. We show that the GaAs-like LO branch of strain-free Ga(As,N) displays a downward frequency shift with increasing y, which confirms that this phonon branch is affected by alloying. In contrast, we find that the GaAs-like TO mode exhibits a slight upward shift with increasing N content. With regard to the GaN-like LO mode, we find that this mode blueshifts with increasing y in the unstrained epilayers. The observed blueshift is larger than previously observed in biaxially strained Ga(As,N).

We discuss the origin of the alloying-induced frequency shifts observed in our strain-free Ga(As,N) samples. We

[a)]Electronic mail: lartus@ija.csic.es

show that the reduction of the number of Ga–As bonds due to the incorporation of substitutional N together with the presence of N-related disorder may account for the observed reduction of the GaAs-like TO-LO splitting. The role of ionic plasmon coupling between the GaAs and GaN sublattices of Ga(As,N) on the frequency of the LO phonon modes is also discussed. We conclude that long-range effects dominate the phonon behavior of the GaAs-like LO branch of Ga(As,N).

II. EXPERIMENTAL DETAILS

Strain-free, 1.5-μm-thick $GaAs_{1-y}N_y$ layers with $y=0.05\%$, 0.1%, 0.2%, 0.7%, and 1.5% were grown by MBE on (100)-GaAs substrates. The composition of the samples was checked by low-temperature photoluminescence (PL), while the relaxed strain state of the films was confirmed by low-temperature photoreflectance (PR) measurements, which did not show any of the strain-related features that appear in Ga(As,N) or (In,Ga)(As,N) grown pseudomorphically on GaAs.[9,10]

Raman measurements were excited at room temperature and at 80 K with the 514.5 nm line of an Ar^+ laser. The spectra were recorded with a Jobin-Yvon T64000 Raman spectrometer equipped with a charge coupled device (CCD) detector. The experiments were performed on a (100) face by using either the double subtractive or the triple additive configuration of the spectrometer with 100 μm slits. To obtain a higher accuracy in the measurement of the frequency of the GaAs-like TO modes of Ga(As,N) as a function of composition, we carried out Raman measurements with the samples tilted about 60° off-normal incidence. With this procedure, the selection rules for the TO phonon modes of zinc-blende semiconductors, forbidden in backscattering on a (100) face, are circumvented, and thus the intensity of the TO peaks is enhanced (see, for instance, Ref. 11). The measurements in off-normal incidence were performed at room temperature by using the triple additive configuration of the spectrometer and 100 μm slits.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical room-temperature Raman spectrum of the strain-free $GaAs_{1-y}N_y$ epilayers studied in this work ($y=0.7\%$). As in the case of coherently grown Ga(As,N) thin films,[1,2,5] the spectrum of the unstrained sample is dominated by the GaAs-like LO mode located at $\sim$290 cm^{-1}. The forbidden GaAs-like TO mode, centered at 269 cm^{-1}, is also observed in the spectrum of the strain-free sample. On the low-frequency tail of the TO peak we observe a weak shoulder at $\sim$255 cm^{-1} that has been previously attributed to the TO(X) phonon mode, activated by disorder.[5] Second-order features appear in the 300–400 and 480–600 cm^{-1} ranges.[1] As in the case of the strained Ga(As,N), we observe the GaN-like LO mode at $\sim$470 cm^{-1}.[1,5]

Next, we carry out a detailed analysis of the frequency behavior of the different first-order optical modes of strain-free, dilute Ga(As,N). We will pay special attention to the TO-LO splitting of the GaAs-like phonon modes.

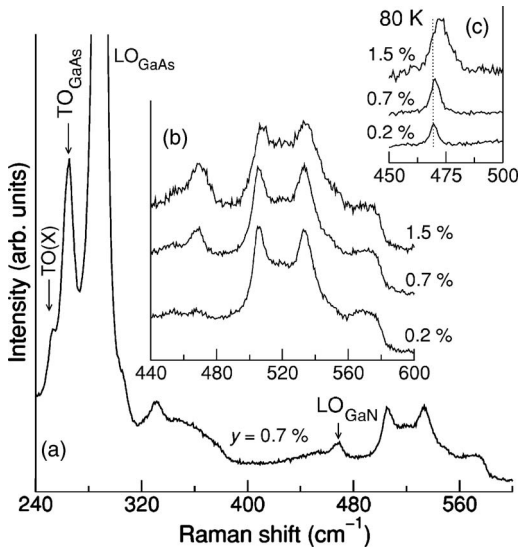

FIG. 1. (a) Raman spectrum of a relaxed $GaAs_{1-y}N_y$ epilayer acquired at room temperature ($y=0.7\%$). (b) Detailed spectra, acquired at room temperature, showing the second-order optical peaks and the evolution of the GaN-like LO mode with increasing y of three different $GaAs_{1-y}N_y$ epilayers ($y=0.2\%$, 0.7%, and 1.5%). (c) Detailed spectra, acquired at 80 K, showing the evolution of the GaN-like LO mode with increasing y of three different $GaAs_{1-y}N_y$ epilayers ($y=0.2\%$, 0.7%, and 1.5%).

A. GaN-like LO mode

Figure 1(b) shows the 440–600 cm^{-1} spectral region for our $GaAs_{1-y}N_y$ samples with higher N content ($y=0.2\%$, 0.7%, and 1.5%). The spectra were acquired at room temperature. Besides the second-order optical peaks above 480 cm^{-1}, the GaN-like LO mode at $\sim$470 cm^{-1} is visible in all spectra, even in the case of the sample with $y=0.2\%$. As expected, the intensity of this peak increases with increasing y.

As can be seen in Fig. 1(b), the GaN-like LO mode gives rise to a weak and broad feature for all samples, in particular, for the sample with $y=0.2\%$. As a consequence, it was not possible to measure with high accuracy the frequency of this mode from the room-temperature spectra. In order to determine the composition dependence of the GaN-like mode in our samples, we carried out Raman measurements at 80 K. In Fig. 1(c) we plot the spectral region at 80 K of the GaN-like LO mode for the samples with $y=0.2\%$, 0.7%, and 1.5%. For $y<0.2\%$, the GaN-like mode was not observed. As expected, the peaks are much sharper at low temperature, enabling us to measure their frequency position. As is clear from Fig. 1(c), the peak for the sample with $y=1.5\%$ is blueshifted, around 3 cm^{-1}, with respect to that of the sample grown with $y=0.2\%$. From a linear fit to the frequency of the GaN-like LO peaks of these three samples, we obtain the following composition dependence for this mode in relaxed Ga(As,N):

$$\omega(\mathrm{LO_{GaN}})\ (\mathrm{cm^{-1}}) = (470 \pm 1) + (2.5 \pm 0.5)y(\%), \qquad (1)$$

where the $y=0$ value corresponds to the frequency of the Ga–N impurity mode in bulk GaAs at 80 K. Although more samples would be required to reduce the error of the slope thus obtained, our results already indicate that the blueshift of the GaN-like LO mode in the strain-free samples

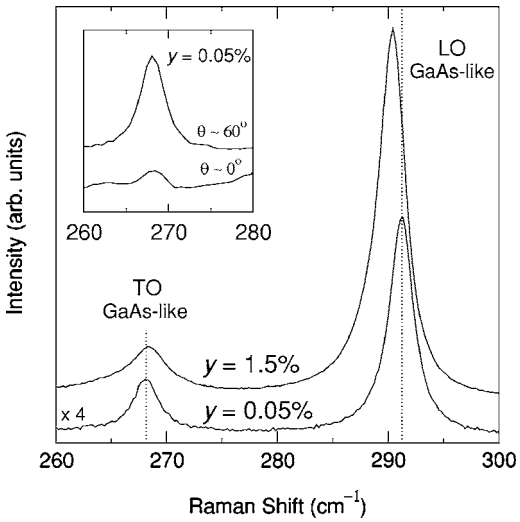

FIG. 2. Room-temperature Raman spectra of two $GaAs_{1-y}N_y$ epilayers, with $y=0.05\%$ and $y=1.5\%$, acquired off-normal incidence to enhance the intensity of the TO peaks. Inset: detail of the TO peak for the $GaAs_{1-y}N_y$ epilayer with $y=0.05\%$, acquired in backscattering configuration ($\theta\sim 0°$) and off-normal incidence ($\theta\sim 60°$).

$[2.5y(\%)\ \mathrm{cm}^{-1}]$ is larger than that found in previous works on strained epilayers. While in Ref. 1 the observed blueshifts were of about $1.97y(\%)\ \mathrm{cm}^{-1}$ for $y\lesssim 3\%$, shifts of $\sim 1.53y(\%)\ \mathrm{cm}^{-1}$ for $y\lesssim 2\%$ were found in Ref. 5. It may be noted that the frequency dependence observed in Ref. 5 above $y\sim 3\%$ was not linear, which may be due to the presence of biaxial strain in the samples or to the effect of nonsubstitutional N in the crystal lattice.

B. GaAs-like optical modes

In backscattering configuration from a (100) face of a zinc-blende compound, the LO modes are allowed and the TO modes are forbidden. Accordingly, the GaAs-like TO peak is very weak in the Ga(As,N) samples with lower N content; only in the samples with higher N content are the GaAs-like TO peaks clearly visible due to a disorder-induced relaxation of the selection rules. To study simultaneously the frequency behavior of the GaAs-like TO and LO modes in all our samples, we carried out Raman measurements with the samples tilted about 60° off-normal incidence to circumvent the selection rules for the TO phonons. We plot in Fig. 2 the corresponding spectra for the $GaAs_{1-y}N_y$ epilayers with $y=0.05\%$ and 1.5%. In the two curves, acquired at room temperature, both the GaAs-like TO ($\sim 268\ \mathrm{cm}^{-1}$) and LO modes ($\sim 290\ \mathrm{cm}^{-1}$) are visible. The spectrum of the sample with $y=0.05\%$ is virtually identical to that of undoped GaAs. To illustrate the relaxation of the selection rules for the TO mode when the spectra are acquired off-normal incidence, we plot in the inset of Fig. 2 two Raman spectra of the sample with $y=0.05\%$, in the frequency region of the TO peak, acquired in normal incidence (i.e., in backscattering geometry) and with the sample tilted about 60° off-normal incidence. The figure shows the sizeable intensity increase of the TO peak achieved when the sample is tilted. The weak intensity of the TO peak in backscattering geometry is a consequence of the good crystal quality of this sample. As expected, the frequency of the TO peaks remains unchanged regardless of the incidence angle.

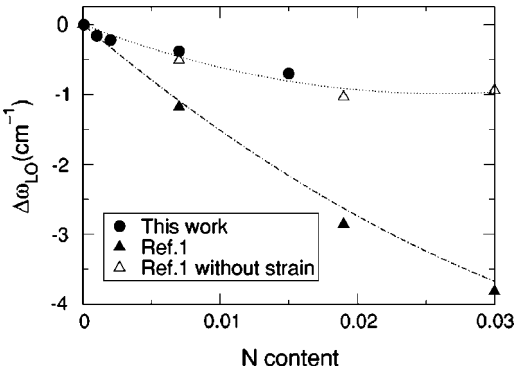

FIG. 3. Frequency of the GaAs-like LO mode obtained from the Raman spectra of our $GaAs_{1-y}N_y$ epilayers (closed circles). For comparison purposes, the LO frequencies measured by Prokofyeva *et al.* in Ref. 1 on coherently strained Ga(As,N) samples are also plotted with closed triangles. The open triangles show the corresponding LO frequency values obtained by subtracting the strain-induced shifts from the experimental values of Ref. 1.

As can be observed in Fig. 2, the LO peak of the sample with $y=1.5\%$ is shifted to lower frequencies, around $0.7\ \mathrm{cm}^{-1}$, with respect to the sample with $y=0.05\%$. This result, which we obtain in strain-free samples, confirms that alloying effects in Ga(As,N) redshift the GaAs-like LO phonon mode. We plot in Fig. 3 the frequency of the GaAs-like LO mode measured in all our samples (closed circles). The figure shows the progressive redshift of this mode with increasing y in the relaxed epilayers. From a linear fit to these data, we obtain the following composition dependence for the GaAs-like LO mode in relaxed Ga(As,N) ($y\lesssim 1.5\%$):

$$\omega(\mathrm{LO}_{\mathrm{GaAs}})\ (\mathrm{cm}^{-1}) = (290\pm 1) - (0.42\pm 0.05)y(\%). \quad (2)$$

The shift that we obtain is virtually identical to that found in Ref. 1, where the redshift component attributed to alloying effects (i.e., after subtraction of the strain effects originated by the pseudomorphic growth of the samples) was estimated to be around $-0.4y(\%)\ \mathrm{cm}^{-1}$ for $y\lesssim 3\%$. For comparision purposes, we have also plotted in Fig. 3 the LO frequencies measured by Prokofyeva *et al.*[1] on strained Ga(As,N) epilayers grown on GaAs (closed triangles), together with the corresponding LO frequency values obtained by subtracting from the experimental frequencies the strain-induced shifts (open triangles). As explained in Ref. 1, the strain-induced shifts amount to approximately $-0.96y(\%)\ \mathrm{cm}^{-1}$, as estimated from biaxial-strain effects in Ga(As,N) epilayers coherently grown on GaAs substrates. Figure 3 shows that the experimental LO frequencies measured in our samples and those of Ref. 1 are in good agreement once the biaxial-strain effects are taken into account.

From the spectra acquired under off-normal incidence (Fig. 2), we find that for the sample with $y=1.5\%$ the GaAs-like TO mode is scarcely blueshifted, around $0.3\ \mathrm{cm}^{-1}$, with respect to the sample with $y=0.05\%$. This result is in agreement with the upward frequency shift expected for the GaAs-like TO frequency of strain-free dilute $GaAs_{1-y}N_y$ with increasing y due to the smaller size of N atoms (i.e., smaller

interatomic distances in $GaAs_{1-y}N_y$ with increasing y should yield tighter spring constants). Whereas no data on the TO phonon frequencies of Ga(As,N) were provided in Refs. 1 and 5, in Ref. 7 it was reported that the GaAs-like TO mode does not show any measurable shift with composition in coherently grown epilayers. In contrast, a very small redshift, which could be attributed to biaxial-strain effects, was observed in Ref. 2. With regard to this, we would like to remark that the determination of the frequency of the GaAs-like TO peaks performed in the previous works was hampered by the fact that this mode is forbidden due to the selection rules, giving rise to weak, broad features in the Raman spectra. As discussed above, here we have overcome this limitation by performing the experiments under off-normal incidence.

C. GaAs-like TO-LO splitting

Our measurements reveal that the TO-LO splitting for the GaAs-like optical modes in strain-free $GaAs_{1-y}N_y$, $\omega(LO_{GaAs})-\omega(TO_{GaAs})$, is reduced by about 1 cm^{-1} from $y=0.05\%$ to $y=1.5\%$. This result cannot be accounted for by short-range effects (i.e., by a change in the spring constant or disorder effects), because these should affect both TO and LO modes in a similar manner. On the contrary, we have observed that the GaAs-like TO mode exhibits a small blueshift, while the GaAs-like LO mode redshifts with increasing N content.

Some authors have attributed the shifts of the GaAs-like LO mode of Ga(As,N) to disorder and have used the spatial correlation model (SCM), based on finite-size effects on the phonon frequencies,[12] to determine phonon correlation lengths as a function of the N content.[7,13] With regard to this, it should be mentioned that previous works have shown that the SCM fails to explain simultaneously the frequency behavior of the TO and LO peaks in disordered GaAs.[14,15] Despite its usefulness to account for the phonon shifts in microcrystals, the SCM has several limitations. First, the SCM predicts larger confinement-induced frequency shifts for the TO mode than for the LO mode of GaAs, as deduced from Raman scattering results on GaAs/AlAs superlattices.[14,16] However, such TO phonon shifts are not observed experimentally in disordered GaAs.[14,17] In addition, to fit the Raman data with the SCM in disordered GaAs one has to arbitrarily change the phonon amplitude at the boundary of the microcrystalline regions from $1/e$ to $\exp(-4\pi^2)$.[15] An alternative account of the shifts and broadening of the optical phonon Raman peaks of disordered GaAs was provided by Burns *et al.*, who considered both strain effects and a change in the TO-LO splitting due to the presence of vacancies, antisites, and interstitials in order to explain their results in ion-bombarded GaAs.[14] The long-range effects associated with LO phonons (i.e., the macroscopic ionic polarization) may also play an important role in the behavior of the GaAs-like LO branch of Ga(As,N).

Next, we analyze the effect of long-range effects on the frequency of the GaAs-like LO phonon branch of Ga(As,N). For undoped GaAs, the ionic plasma frequency associated with the LO phonons, $\Omega_{GaAs}=(\omega_{LO}^2-\omega_{TO}^2)^{1/2}$, is given by[18,19]

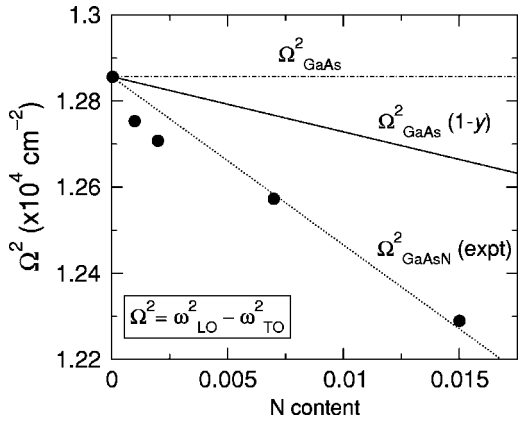

FIG. 4. Squared ionic plasmon frequency, $\Omega^2_{GaAsN}(\text{expt})=\omega^2(LO_{GaAs})-\omega^2(TO_{GaAs})$, associated with the GaAs-like LO mode of Ga(As,N) as determined from the GaAs-like TO and LO frequencies measured in the samples studied in this work (closed circles). For comparison purposes, the progressive reduction of the squared ionic plasmon frequency of the GaAs-like LO mode resulting from the substitution of As by N, i.e., $\Omega^2_{GaAs}(1-y)$, is also plotted. Ω^2_{GaAs} is the squared ionic plasmon frequency for bulk GaAs.

$$\Omega^2_{GaAs}=\frac{4\pi N e^{*2}_{T,GaAs}}{\epsilon_\infty V \mu_{GaAs}}, \tag{3}$$

where ω_{LO} and ω_{TO} are the long-wavelength LO and TO phonon frequencies of bulk GaAs, respectively μ_{GaAs} is the Ga–As reduced mass, $e^*_{T,GaAs}$ is the transverse effective charge for the longitudinal Ga–As oscillators, N is the total number of Ga–As bonds (i.e., N is the number of primitive cells, so there are $2N$ atoms in the GaAs crystal), V is the volume of the crystal ($V=Na_0^3/4$, where a_0 is the lattice parameter of the conventional cell), and ϵ_∞ is the high-frequency dielectric constant of GaAs.

To understand why the TO-LO splitting is reduced in Ga(As,N) with increasing N content, we first note that $\epsilon_\infty(\text{GaAsN})<\epsilon_\infty(\text{GaAs})$, as can be concluded from the corresponding values for GaAs and c-GaN. Thus, the variation of ϵ_∞ cannot explain the observed reduction of Ω_{GaAsN}. Similarly, as expected from the smaller lattice parameter of c-GaN with respect to GaAs, the lattice parameter of Ga(As,N), and therefore the total volume of the crystal, decreases with increasing y,[20] which neither can explain the observed reduction in the TO-LO splittings. On the other hand, it is expected that $e^*_{T,GaAs}$ remains basically unchanged for the Ga–As oscillators within the GaAs sublattice of the Ga(As,N) ternary alloy.[19] This is particularly true in the dilute regime. In contrast, the total number of Ga–As oscillators is reduced when N is incorporated substitutionally into GaAs. In this case, the total number of Ga–As bonds N has to be replaced by $N(1-y)$ in Eq. (3), giving rise to a reduction of the TO-LO splitting.

We plot in Fig. 4 (solid line) the squared ionic plasmon frequency associated with the GaAs-like LO mode of Ga(As,N) that results from considering only substitutional nitrogen, i.e., $\Omega^2_{GaAs}(1-y)$ (here we neglect the changes in ϵ_∞ and a_0, the effects of which are expected to be much smaller than those related to the reduction of the number of oscillators). For comparison, we also plot the squared ionic plasmon frequency as determined from the Raman measurements

in our samples, i.e., $\Omega^2_{GaAsN}(expt)=\omega^2(LO_{GaAs})-\omega^2(TO_{GaAs})$ (closed circles). Surprisingly, the experimental $\Omega^2_{GaAsN}(expt)$ values are appreciably lower than $\Omega^2_{GaAs}(1-y)$ (see Fig. 4). Consequently, most of the TO-LO splitting reduction (and therefore most of the LO phonon shifts) that we observe in our samples still remain to be explained. By subtracting $\Omega^2_{GaAs}(1-y)$ from $\Omega^2_{GaAsN}(expt)$ in Fig. 4, we find that the deviation between the experimental data and the theoretical TO-LO splitting, obtained assuming only substitutional N, is $\Delta\Omega^2=\Omega^2_{GaAsN}(expt)-\Omega^2_{GaAs}(1-y)\approx -0.02\Omega^2_{GaAs}y(\%)$; this amounts to more than 60% of the total TO-LO splitting reduction observed in our samples.

Here, we speculate that the fraction of $\Omega^2_{GaAsN}(expt)$ reduction that remains to be explained may be attributed to the presence of defects (interstitials, vacancies, and antisites). Such defects were shown to give rise to a sizeable reduction of Ω^2_{GaAs} in disordered GaAs.[14] Following the arguments of Burns *et al.*,[14] we find that a ratio of vacancies (antisites) to atoms of ~0.5% (~0.3%) in the sample with $y=1.5\%$ may account for our Raman data. With regard to this, one should keep in mind that dilute nitrides contain a high density of defects, mainly N interstitials, Ga vacancies, and N clusters, which are responsible for the low luminescence efficiency of the as-grown materials.[21,22] Thus, it is likely that a combination of such defects lowers the total number of Ga–As oscillators and/or changes the high-frequency dielectric constant of the material, giving rise to an important part of the observed LO phonon shifts.

Finally, we consider the effect of ionic plasmon coupling on the frequency of the GaAs-like LO mode of Ga(As,N), which may also explain part of the shifts observed for this phonon mode. As it is well known, the LO phonon branches of ternary alloys may display appreciable bowings as a consequence of the long-range Couloumb interactions involved in the long-wavelength LO phonons. This is the case, for instance, of (In,Ga)As.[19] Accordingly, it cannot be ruled out that the behavior of the GaAs-like LO mode of Ga(As,N) be a consequence of the electrostatic coupling between the GaAs and GaN sublattices of this compound, yielding a downward (upward) frequency shift of the GaAs-like (GaN-like) LO mode. To test this hypothesis we used the repulsion model outlined in Ref. 19, which allows one to determine the LO frequencies of ternary alloys without any adjustable parameters, in order to estimate the effect of ionic plasmon coupling on the GaAs-like LO branch of $GaAs_{1-y}N_y$. This model has successfully accounted for the LO phonon behavior[19] and LO-plasmon coupling phenomena[23,24] in (In,Ga)As ternary alloys. For the calculations, which we restricted to the dilute regime, we used the following data: for the GaAs-like TO branch of Ga(As,N), we used the experimental frequency dependence, as obtained from Fig. 2; and for the GaN-like branches, we used Vegard's law together with the frequency of the TO and LO modes of *c*-GaN (555 and 742 cm^{-1}, respectively) and the frequency of the Ga–N impurity mode in GaAs (470 cm^{-1}). Our analysis indicates that only around 10% of the reduction of the TO-LO splitting observed in our samples may be originated by coupling between the two polar sublattices. Thus, we conclude that the observed TO-LO splitting reduction in dilute Ga(As,N) is primarily due to the reduction in the number of Ga–As bonds caused by the substitutional N and by the increased amount of point defects and clusters induced by the presence of N.

IV. CONCLUSIONS

We have used Raman scattering to investigate the behavior of the optical phonons of unstrained, dilute $GaAs_{1-y}N_y$ ($y\lesssim 1.5\%$), where the phonon frequency shifts can be solely attributed to alloying effects. We find that the GaN-like LO mode blueshifts with increasing *y* in the strain-free epilayers. The observed shifts, of about $2.5y(\%)$, are higher than those previously observed in strained samples. In turn, we have found that the GaAs-like LO mode in unstrained $GaAs_{1-y}N_y$ exhibits a downward frequency shift with increasing *y*. The observed redshift amounts to about $-0.42y(\%)$, in good agreement with previous estimations of the alloying effect in strained epilayers.

Given that the frequency of the GaAs-like TO mode does not change significantly in this composition range, the redshift of the GaAs-like LO mode cannot arise from short-range effects. The observed shifts imply an appreciable reduction of the GaAs-like TO-LO splitting that cannot be explained solely by the reduction of Ga–As oscillators due to the substitution of As ions by N ions. A disorder-induced reduction of the number of Ga–As oscillators that contributes to the long-range effects and a minor contribution of ionic plasmon coupling between the GaAs and GaN sublattices of Ga(As,N) may account for the observed behavior of the GaAs-like LO mode of this material. We conclude that long-range effects determine the behavior of the GaAs-like LO mode of dilute Ga(As,N).

ACKNOWLEDGMENTS

This work was supported by the Spanish Ministry of Science and Technology (Contract No. MAT2004-0664 and Ramon y Cajal Program). We would like to thank Amalia Patanè for the PL and PR data.

[1] T. Prokofyeva, T. Sauncy, M. Seon, M. Holtz, Y. Qiu, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **73**, 1409 (1998).
[2] A. M. Mintairov, P. A. Blagnov, V. G. Melehin, N. N. Faleev, J. L. Merz, Y. Qiu, S. A. Nikishin, and A. Temkin, Phys. Rev. B **56**, 15836 (1997).
[3] M. J. Seong, A. Mascarenhas, and J. F. Gaisz, Appl. Phys. Lett. **79**, 1297 (2001).
[4] M. J. Seong, M. C. Hanna, and A. Mascarenhas, Appl. Phys. Lett. **79**, 3974 (2001).
[5] A. Mascarenhas and M. J. Seong, Semicond. Sci. Technol. **17**, 823 (2002).
[6] J. Wagner, T. Geppert, K. Köhler, P. Ganser, and N. Herres, J. Appl. Phys. **90**, 5027 (2001).
[7] H. F. Liu, N. Xiang, S. Tripathy, and S. J. Chua, J. Appl. Phys. **99**, 103503 (2006).
[8] M. Reason, X. Weng, W. Ye, D. Dettling, S. Hanson, G. Obeidi, and R. S. Goldman, J. Appl. Phys. **97**, 103523 (2005).
[9] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **61**, 4433 (2000).
[10] J. Ibáñez, R. Kudrawiec, J. Misiewicz, M. Schmidbauer, M. Henini, and M. Hopkinson, J. Appl. Phys. **100**, 093522 (2006).
[11] L. Artús, R. Cuscó, J. Ibáñez, N. Blanco, and G. González-Díaz, Phys. Rev. B **60**, 5456 (1999).
[12] H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39**, 625 (1981).
[13] E. K. Koh, Y. J. Park, E. K. Kim, S. Min, and S. H. Choh, Phys. Rev. B **57**, 11919 (1998).
[14] G. Burns, F. H. Dacol, C. R. Wie, E. Burstein, and M. Cardona, Solid State

Commun. **62**, 449 (1987).
[15]I. H. Campbell and P. M. Fauchet, Solid State Commun. **58**, 739 (1986).
[16]A. K. Sood, J. Menendez, M. Cardona, and K. Ploog, Phys. Rev. Lett. **54**, 2111 (1985).
[17]K. Tiong, P. M. Amirtaraj, F. Pollak, and D. E. Aspnes, Appl. Phys. Lett. **44**, 122 (1984).
[18]G. Lukovsky, R. M. Martin, and E. Burstein, Phys. Rev. B **4**, 1367 (1971).
[19]J. Groenen, R. Carles, G. Landa, C. Guerret-Piécourt, C. Fontaine, and M. Gendry, Phys. Rev. B **58**, 10452 (1998).
[20]See, for instance, W. J. Fan, S. F. Yoon, T. K. Ng, S. Z. Wang, W. K. Loke, R. Liu, and A. Wee, Appl. Phys. Lett. **80**, 4136 (2002), and references therein.
[21]W. Li, M. Pessa, T. Ahlgren, and J. Decker, Appl. Phys. Lett. **79**, 1094 (2001).
[22]J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Oila, and K. Saarinen, Appl. Phys. Lett. **82**, 40 (2003).
[23]R. Cuscó, L. Artús, S. Hernández, J. Ibáñez, and M. Hopkinson, Phys. Rev. B **65**, 035210 (2002).
[24]J. Ibáñez, E. Tarhan, A. K. Ramdas, S. Hernández, R. Cuscó, L. Artús, M. R. Melloch, and M. Hopkinson, Phys. Rev. B **69**, 075314 (2004).